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Microstructures of Carnonaceous Materials within Illite of the Daedong Group Slate from Jeongok Area, Korea

전곡지역 대동층군 점판암의 일라이트내에 협재된 탄질물의 미세구조

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ABSTRACT : Microstructures of carbonaceous materials, occurring in a carbonaceous slate of the Daedong Group from Jeongok area, were investigated using high-resolution transmission electron microscopy (HRTEM). Carbonaceous materials are in an early stage of graphitization, and occur as extremely thin (<100 Å) domains both between and intergrown within illite crystals. These materials, in places, approach graphite in their structural ordering. Carbonaceous layers are wavy, discontinuous, and partly circular, resulting in a "fingerprint" texture. Such characteristics are typical of poorly graphitized materials, which have abundant defects and limited structural integrity. These interstratified materials could have been trapped during the growth of illite or have been inherited from precursor clay minerals in the host sediments during diagenesis and low-grade metamorphism. The fine-scale interstratification within illite indicates that graphitization of carbonaceous materials in low-grade rocks involves complicated microstructural changes. Heterogeneous microstructure of carbonaceous materials suggests that the graphitization process in metamorphic rocks would experience discontinuous steps until carbonaceous materials are homogenized as discrete domains at high temperature. Furthermore, this study shows that undisrupted structures and textures of fine-grained carbonaceous materials can be investigated by utilizing ion-milled specimens.

Keyword : carbonaceous material, high-resolution transmission electron microscopy (HRTEM), microstructure, illite

요약 : 이 연구에서는 대동층군 탄질 점판암내에 산출하는 탄질물의 미세구조를 고분해능 투과전자현미경 (HRTEM)을 이용하여 조사하였다. 관찰된 탄질물은 구조가 부분적으로 흑연화된 흑연화과정의 초기단계 물질로서 100 Å 이하의 매우 얇은 크기로 일라이트 결정들의 경계면 사이나 일라이트 결정내에 협재되어 나타난다. 탄질물의 층상구조는 휘어있거나 불연속적이며, 부분적으로 원형조직을 보이는 "지문" 조직을 이루고 있다. 이러한 특징은 많은 결함구조를 가지고 구조적으로 충분히 흑연화되지 않은 물질에서 볼 수 있는 전형적인 구조다. 미세한 규모로 협재된 조직을 보이는 탄질물은 퇴적물의 속성작용과 저변성작용시 일라이트가 성장하는 동안에 포획되었거나, 또는 일라이트 이전의 점토광물내에 흡착되었던 물질들로부터 유래된 것으로 보인다. 이처럼 탄질물과 일라이트가 미세한 규모로 협재되어 산출하는 특징은 저변성암에서 일어나는 흑연화작용시 복잡한 미세구조의

변화가 수반되었음을 지시한다. 다양한 미세구조를 보여주는 흑연질 물질의 산출은 탄질물이 고온에서 균질한 흑연으로 생성되기까지 불연속적인 단계를 거쳐 반응할 가능성을 지시한다. 끝으로, 이 연구는 이온 빔을 이용하여 제작한 시료를 관찰함으로써 암석내에 함유된 탄질물들의 조직을 훼손하지 않고 관찰할 수 있음을 보여준다.

주요어 : 탄질물, 고분해능 투과전자현미경 (HRTEM), 미세구조, 일라이트

Introduction

Carbonaceous material occurs as various forms in terrestrial (French, 1964; Jedwab, 1984; Buseck and Huang, 1985; Ross and Bustin, 1990) and extraterrestrial materials (Smith and Buseck, 1981; Wopenka, 1988). Much terrestrial carbonaceous material was derived from early organisms, and ranges from kerogen and coal to highly ordered graphite. Extensive investigations have been carried out by many workers using X-ray diffraction (XRD) (Landis, 1971; Wada *et al.*, 1994), high-resolution transmission electron microscopy (HRTEM) (Buseck and Huang, 1985; Buseck *et al.*, 1988; Oh *et al.*, 1991), and Raman spectroscopy (Tuinstra and Koenig, 1970; Wopenka and Pasteris, 1993; Yui *et al.*, 1996) to elucidate the graphitization process, and it has been revealed that carbonaceous materials progressively increase in crystallinity, evolving towards graphite with metamorphism.

Carbonaceous materials within low-grade metamorphic rocks commonly coexist with other sheet silicates, which are likely to experience metamorphic changes in close association with carbonaceous materials. However, previous HRTEM, XRD, and Raman spectroscopic studies aimed at observing the crystallinity and structural characteristics are based on materials disaggregated from their host rocks. Such sample preparation resulted in the loss of textural and crystallographic integrity of the matrix minerals. However, we found that undisrupted *in situ* textural and structural states of carbonaceous materials can be profitably investigated by utilizing ion-milled specimens in HRTEM study.

Noncrystalline and poorly crystalline carbonaceous material tends to aromatize with temperature and time, producing planar structures (Buseck and Huang, 1985; Buseck *et al.*, 1988). Clay minerals also have planar structures, so there is at least the possibility that the two minerals could form in intergrowth with their basal planes parallel to each other. In order to explore this possibility, we investigated a carbonaceous slate of the Late Triassic - Early Jurassic Daedong Group from the Jeongok area, Korea (Yu *et al.*, 1992), which was subjected to subgreenschist facies metamorphism. Our observations of undisrupted specimens from the slate confirm that some carbonaceous materials are intimately interstratified within illite crystals rather than occurring entirely as discrete crystallites.

Experimental Method

Thin sections retaining the original textural integrity of the host slaty rocks were prepared with orientations perpendicular to the foliation. Following optical and electron microprobe observations, 3-mm washers were attached to selected areas. Washer-mounted specimens were ion-milled, lightly coated with carbon, and examined at 400 kV with a JEOL JEM-4000EX transmission electron microscope equipped with a top-entry stage having tilting angles of ±15°, a spherical aberration coefficient (C_s) of 1.0 mm, and a structure resolution of 1.7 Å (Smith *et al.*, 1986). A 40-μm objective aperture and a 150-μm condenser aperture were used for high-resolution TEM imaging.

Results

HRTEM investigation shows that carbonaceous material occurs primarily as thin domains, which are approximately 100 Å thick, between illite crystals (Fig. 1). Carbonaceous layers lie parallel, in most instances, to the neighboring illite layers (Fig. 2a), but high-angle boundaries between them are occasionally observed (Fig. 2b). Its interplanar spacings vary slightly, and lattice fringes are somewhat wavy and discontinuous along the layers.

HRTEM observations also show that carbonaceous material occurs in part as thin crystallites inside illite crystals. Stacks of carbonaceous layers are observed to be distributed along (001) of illite in otherwise structurally homogeneous illite crystals (Fig. 3). Most interstratified carbonaceous materials are a few tens of Å thick, and aligned parallel to the illite layers. Interstratified carbonaceous layers are generally extended laterally as partly wavy layers, and they exhibit in general better parallelism with illite and are thinner than the carbonaceous material at the grain boundaries. Single carbonaceous layers within illite were not discerned with certainty, but narrow stacks of carbonaceous layers could be distinguished from the sublayers of illite based on the 10-Å periodicities that are characteristic of the illite

Fig. 1. HRTEM image showing carbonaceous material between the boundaries of illite crystals. Carbonaceous material shows wavy layer structure and edge dislocations.

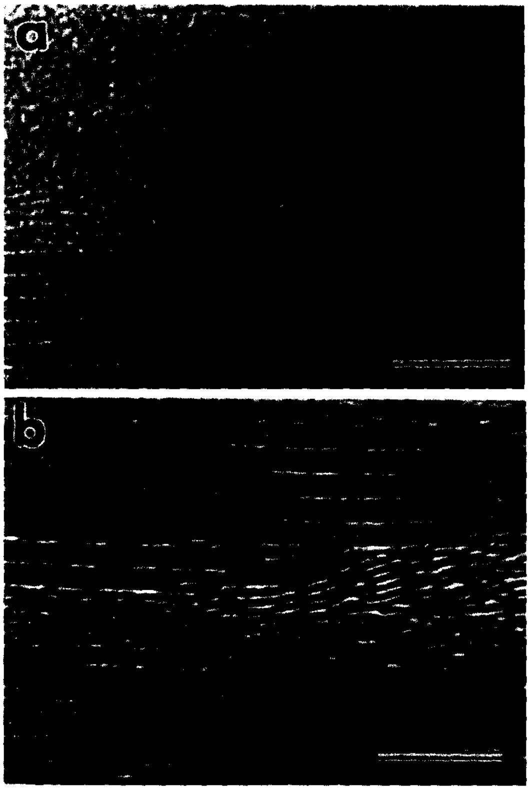

Fig. 2. The boundaries between illite and carbonaceous material are parallel (a) or oblique to the illite layers (b). The scale bars of both images indicate 50 Å.

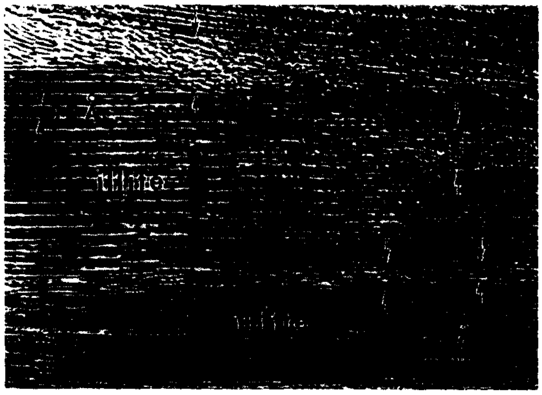

Fig. 3. HRTEM image showing stacks of carbonaceous layers interstratified within an illite crystal. Single illite layers with 10-Å periodicity are resolved into three parallel sublayers. Discernible thin stacks of interstratified carbonaceous layers are marked by arrows.

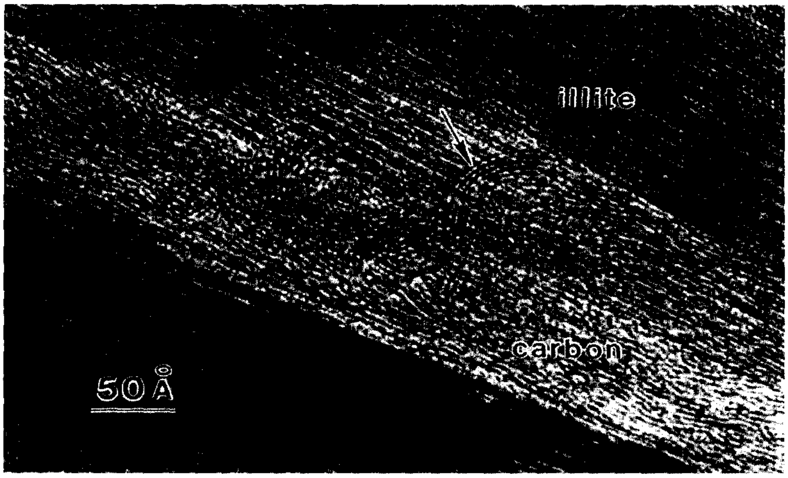

Fig. 4. HRTEM image showing partly circular form of carbonaceous layers (marked by an arrow) intergrown within an illite crystal.

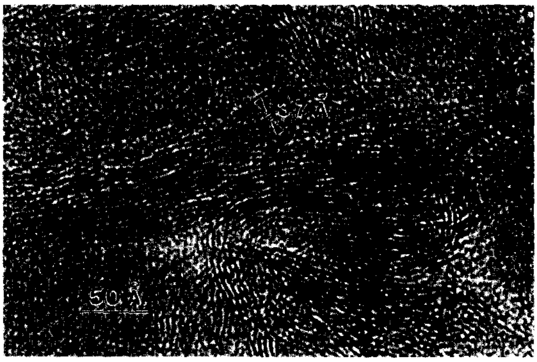

Fig. 5. HRTEM image of discrete carbonaceous material showing a "fingerprint" texture. Carbonaceous layers are wavy and circular in part.

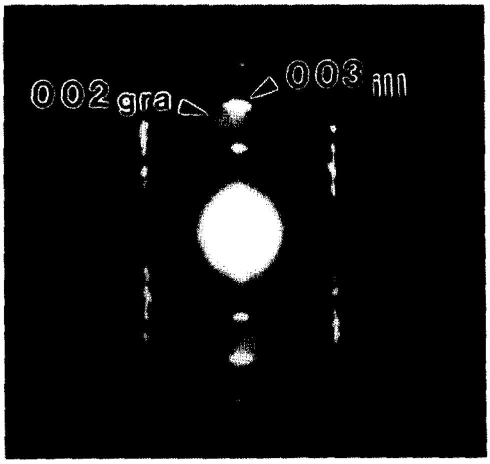

Fig. 6. SAED pattern obtained from poorly graphitized material and illite. The 002 of carbonaceous material and 003 of illite are marked as 002_{gra} and 003_{ill}, respectively. Weak reflections from the carbonaceous material are slightly circular and diffuse.

structure.

Carbonaceous materials occur primarily as linear aggregates of parallel layers, but some of them show a circular structure (Fig. 4). However, the circular characteristics are not perfect; circular layers trend toward linear layers. Isolated carbonaceous materials in the matrix of slate samples exhibit a texture that lacks parallelism between the constituent stacks of carbonaceous layers (Fig. 5). Carbonaceous layers are wavy and somewhat circular in part, and most layers are discontinuous along layers, resulting in a "fingerprint" texture. Such micro structures are typical of poorly graphitized materials, which have abundant defects and limited structural integrity (Buseck and Huang, 1985; Buseck *et al.*, 1988; Oh *et al.*, 1991).

Selected-area electron diffraction patterns of carbonaceous materials show that the only discernable reflection spots of the material occur near the 003 reflection of illite and they are extremely weak and diffuse (Fig. 6). Such diffuseness of reflection spots is consistent with the poor structural ordering of the carbonaceous material. The reflections are tentatively indexed as corresponding to 002 of graphite. The interplanar spacings of the carbonaceous material are variable in HRTEM images (Figs. 1, 2, 3, and 5), but the diffraction pattern suggests an average (002) interplanar spacing of approximately 3.7 Å (Fig. 6).

Discussion

The graphitization process can be affected by many factors, such as temperature, pressure, metamorphic fluid, and the lithology of host rocks (Landis, 1971; Wopenka and Pasteris, 1993; Wada *et al.*, 1994; Yui *et al.*, 1996). Also, the types of precursor organic matter in the original sediments may influence the graphitization in low-grade metamorphic rocks (Buseck and Huang, 1985; Wopenka and Pasteris, 1993; Yui *et al.*, 1996). Occurrence of poorly crystalline carbonaceous material indicates the effect of low-grade metamorphism, and the presence of carbonaceous materials with various microstructures, such as circular and linear structures (Figs. 4 and 5), suggests that distinct varieties of precursor organic matters could have been existent in the original sediments (Tissot and Welte, 1984).

The degree of graphitization is commonly evaluated by the structural parameters, d(002) and L_c, which represent the spacings between the stacked layers and the crystal thickness along the c axis, respectively; d(002) gradually decreases and L_c increases with metamorphism (Landis, 1971; Grew, 1974; Itaya, 1981; Wopenka and Pasteris, 1993; Wada *et al.*, 1994). The average d(002) value of 3.7 Å determined in this study is considerably higher than 3.35 Å, the value of graphite. The host rock was subjected to subgreenschist-facies metamorphism, and the relatively large d(002) value and thin crystallites are consistent with such low-grade metamorphism. Moreover, disordered structural features observed in the lattice-fringe images confirm that the carbonaceous material is poorly graphitized (Figs. 1, 3, 4, and 5).

Interstratified carbonaceous material is likely to be less accessible to metamorphic fluids, and therefore its structural evolution and crystal growth are likely to be more sluggish than that of carbonaceousc material at grain boundaries or in the matrix. Previous XRD studies indicate that the decrease in d(002) of carbonaceous matter in metamorphic rocks is slow until the temperature reaches approximately 400℃ (Wada *et al.*, 1994; Yui *et al.*, 1996), which is the approximate upper limit of greenschist-facies metamorphism. Interstratified carbonaceous material would be eventually segregated from illite crystals, to form discrete carbonaceous particles with the progress of metamorphism. These particles easily exposed to intergranular metamorphic fluids would certainly be subjected to faster graphitization, as found in high-grade rocks. Graphitization would be facilitated once the interstratified carbonaceous layers are segregated from illite or mica crystals in high-grade rocks.

There has been disagreement about whether graphitization is a continuous process or it involves stepwise changes (Landis, 1971; Grew, 1974; Itaya, 1981; Wopenka and Pasteris, 1993). The occurrence of interstratified carbonaceous layers as well as isolated carbonaceous materials suggests that the graphitization process would experience rather discontinuous steps until interstratified carbonaceous layers are segregated from micas to be homogenized as discrete domains at high temperature. This interpretation is compatible with the Raman spectroscopic study suggesting that the graphitization at low temperature differs among various carbonaceous materials until some degree of graphitization is attained (Wopenka and Pasteris, 1993). Furthermore, step-wise changes may develop during the graphitization, because the process is kinetically controlled and in general lacks the equilibrium relationship in low-grade metamorphic rocks.

Another question is how carbonaceous material initially formed as intercalates within illite crystals. The majority of illite in pelitic rocks generally evolves from smectite during diagenesis and low-grade metamorphism of the sediments (Lee *et al.*, 1985; Peacor, 1992), concomitant with an increase in crystallinity and crystal size. Illite or precursor smectite could grow by coalescence of individual crystals during diagenesis and metamorphism, and their platy shape is likely to influence other crystals to form passively oriented boundaries parallel to the planar surfaces. If small units of carbonaceous material were trapped between such boundaries, they would appear as intercalated layers within the resultant illite crystals.

Alternatively, interstratification of carbonaceous material could result from the absorption capability of smectite. Smectite, which evolves toward illite and eventually muscovite through diagenesis and metamorphism, can absorb a variety of organic molecules as well as alkali cations in its interlayers (Bandosz *et al.*, 1992; Wilson *et al.*, 1992); experimental studies indicate that carbonaceous molecules can be introduced into the interlayer space of smectite (Green-Kelly, 1955; Sonobe *et al.*, 1990; Putyera *et al.*, 1994). If smectite containing the absorbed carbonaceous molecules transforms to illite, carbonaceous matters within interlayers could be partially graphitized by dissociating H, O, N, and other atoms, resulting in interstratified carbonaceous material.

Conclusions

Our HRTEM study on a carbonaceous slate of Daedong Group reveals that carbonaceous material can be interstratified within clay minerals in the natural environment. Such interstratification is related to the illitization of clay minerals during diagenesis and metamorphism. Some thin crystallites that were characterized from carbonaceous concentrates separated from host rocks in previous studies may represent carbonaceous material that was actually intergrown within clay minerals. The occurrences of interstratified carbonaceous layers as well as discrete carbonaceous materials suggest that the graphitization process would involve discontinuous steps until carbonaceous materials are segregated to form discrete domains at high temperature. We suggest that the evolution of carbonaceous materials could involve such intergrowth structures and that the graphitization process, especially in low-grade pelitic rocks, can be more complex than previously recognized.

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References

Bandosz, T.J, Jagiello, J., Amankwah, K.A.G. and Schwarz, J. A. (1992) Chemical and structural properties of clay minerals modified by inorganic and organic material. Clay Miner., 27, 435-444.

Buseck, P.R. and Huang, B.J. (1985) Conversion of carbonaceous material to graphite during metamorphism. Geochim. Cosmochim. Acta, 49, 2003-2016.

Buseck, P.R., Huang, B.J. and Miner, B. (1988) Structural order and disorder in Precambrian kerogens. Org. Geochem., 12, 221-234.

French, B.M. (1964) Graphitization of organic material in a progressively metamorphosed Precambrian iron formation. Science, 146, 917-918.

Greene-Kelly, R. (1955) Sorption of aromatic organic compounds by montmorillonite. Pt. 1, orientation studies. Trans. Faraday Soc., 51, 412-424.

Grew, E.S. (1974) Carbonaceous materials in some metamorphic rocks of New England and other areas. J. Geol., 82, 50-73.

Itaya, T. (1981) Carbonaceous material in pelitic schists of the Sanbagawa metamorphic belt in central Shikoku, Japan. Lithos, 14, 215-224.

Jedwab, J. (1984) Graphite crystals in hydrothermal vents. Nature, 310, 41-43.

Landis, C.A. (1971) Graphitization of dispersed carbonaceous material on metamorphic rocks. Contrib. Mineral. Petrol., 30, 34-45.

Lee, J.H., Ahn, J.H. and Peacor, D.R. (1985) Textures in layered silicates: progressive changes through diagenesis and low-grade metamorphism. J. Sed. Petrol., 55, 532-540.

Oh, J.H., Rouzaud, J.N., Oberlin, A. Deurbergue, A. and Kwak, Y.H. (1991) Structural study of graphitization in the Moongyeong coalfield, South Korea. Bull. Soc. Geol. France, 162, 399-407.

Peacor, D.R. (1992) Diagenesis and low-grade metamorphism of shales and slates. Rev. Mineral., 27, 335-380.

Putyera, K., Bandosz, T.J., Jagiello, J. and Schwarz, J.A. (1994) Sorption properties of carbon composite materials formed from layered clay minerals. Clays Clay Miner., 42, 1-6.

Ross, J.V. and Bustin, R.M. (1990) The role of strain energy in creep graphitization of anthracite. Nature, 343, 58-60.

Smith, D.J., Barry, J.C., Bursill, L.A., Petford, A.K. and Wheatley, J.C. (1986) Atomic resolution imaging of crystalline defects and surfaces. JEOL News, 24E, 2-6.

Smith, P.P.K. and Buseck, P.R. (1981) Graphitic carbon in Allende meteorite: a microstructural study. Science, 212, 322-324.

Sonobe, N., Kyotani, T. and Tomita, A. (1990) Carbonization of polyfurfuryl alcohol and polyvinyl acetate between the lamellae of montmorillonite. Carbon, 28, 483-488.

Tissot, B.P. and Welte, D.H. (1984) Petroleum formation and occurrence. Springer-Verlag, New York, 627p.

Tuinstra, F. and Koenig, J.L. (1970) Raman spectrum of graphite. J. Chem. Phys., 53, 1126-1130.

Wada, H., Tomita, T., Matsuura, K., Iuchi, K., Ito, M. and Morikiyo, T. (1994) Graphitization of carbonaceous matter during metamorphism with reference to carbonate and pelitic rocks of contact and regional metamorphism, Japan. Contrib. Mineral. Petrol., 118, 217-228.

Wilson, P.N., Parry, W.T. and Nash, W.P. (1992) Characterization of hydrothermal tonelitc veins from black shale, Oquirrh Mountains, Utah. Clays Clay Miner., 40, 405-420.

Wopenka, B. (1988) Raman observation on individual interplanetary dust particles. Earth Planet. Sci. Lett., 88, 221-231.

Wopenka, B. and Pasteris, J.D. (1993) Structural characterization of kerogen to granulite-facies graphite: applicability of Raman microprobe spectroscopy. Amer. Mineral., 78, 533-557.

Yu, K.M., Kwon, Y.I. and Chun, H.Y. (1992) Stratigraphy and mineral composition of sandstones from the Daedong Group in Yeoncheon area. J. Geol. Soc. Korea, 28, 152-166.

Yui, T.-F., Huang, E. and Xu, J. (1996) Raman spectrum of carbonaceous material: a possible metamorphic grade indicator of low-grade metamorphic rocks. J. Metamorphic Geol., 14, 115-124.

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